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EP-A- 0 185 918
EP-A- 0 263 718
DE-A- 3 007 418

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EP 0 318 049 B1

Description

The present invention is concerned with new crystalline copolymers of propylene, and with the process for preparing them.

Those skilled in the art know that polypropylene can be modified by introducing small amounts of comonomers, mainly ethylene and 1-butene, during the polymerization reaction. The purpose of this modification is of lowering the melting point of the polymer, and hence obtaining films showing improved characteristics of weldability.

However, the polymers obtained by means of the processes known to date suffer from the drawback of a non-homogeneous distribution of the comonomers; this causes the polymers to show high solubility characteristics in cold xylene, and the manufactured articles obtained from them to have decreased mechanical properties.

From European patent application N. 0 185 918, polymerizing propylene with stereospecific catalysts is known, wherein such stereospecific catalysts are obtained from stereorigid and chiral compounds of zirconium, such as ethylene-bis-indenyl-zirconium dichloride, and ethylene-bis-(4,5,6,7-tetrahydroindenyl)zirconium dichloride, and from methylalumoxanic compounds.

The catalysts are also used in the polymerization of mixtures of propylene with ethylene or other olefins, with copolymers being obtained which, in the examples, are rich of ethylene and are soluble in xylene, and show an isotactic configuration of the propylenic sequences.

No mention is made in the above mentioned EP-A- 0185918 of any advantage of preparing copolymers of propylene containing small amounts of comonomers.

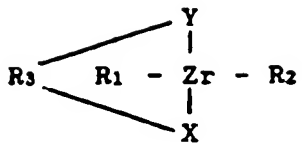
It is also known from JP-A-62121707 to prepare random copolymers of an alpha-olefin, such as propylene, with ethylene, endowed with heat sealability properties.

Said copolymers are prepared in the presence of a catalyst obtained by reacting an aluminooxane with a Group IV B transition metal compound such as ethylenebis(indenyl) dimethylzirconium.

In said Japanese application it is stated that the copolymer may contain up to 99 mol% of alpha-olefin but in the examples the ethylene content is not less than 15 mol%. Therefore, also in JP-A-62121707 there is no indication of particular advantages of preparing copolymers of propylene containing small amounts of comonomers.

The present Applicants have unexpectedly found now that by using catalytic systems obtained from:

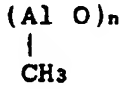
a) a stereorigid and chiral compound of zirconium of formula



wherein:

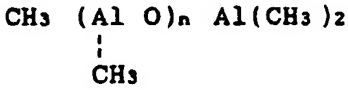
- R_1 and R_2 are halogens or alkyl groups of from 1 to 6 C atoms or hydrogen;
- X and Y are asymmetrical single-ring or multi-ring organic groups;
- R_3 is a linear group of from 1 to 4 C atoms, or a cyclic group containing from 3 to 6 C atoms;

b) an alumoxanic compound of formula



with n being comprised within the range of from 2 to $\bar{2}5$;

or



with n being comprised within the range of from 1 to $\bar{2}5$;

propylene copolymers with minor amounts of ethylene and/or alpha-olefins

$CH_2 = CHR$

wherein R is an alkyl radical of from 2 to 20 C atoms, which are endowed with a high crystallinity, and with very good mechanical properties (very similar to propylene homopolymer), have a melting point comprised within the range of from 110° to 140°C and show a limited solubility in cold xylene (soluble polymer fraction in xylene at 25°C lower than 10 %), can be obtained if the polymerization of the monomers is carried out under conditions under which the formed copolymer has a composition similar to the composition of the monomers present in the gas phase.

In the above general formula of the zirconium compound the following definitions are preferred:

X and Y are preferably indenyl or tetrahydroindenyl;

R_1 and R_2 are preferably Cl or methyl;

R_1 and R_2 can also be hydrogen which is among the preferred ones;
R_3 is preferably $-CH_2CH_2-$.
Specific zirconium compounds are those of the Examples like ethylene-bis-indenyl-$ZrCl_2$ and ethylene-bis(tetrahydroindenyl)-$ZrCl_2$. A preferred alumoxanic compound is that of the Examples (polymethylalumoxane).

The present Applicants have found, and this is an at all unexpected aspect of the present invention, that the composition of the copolymers is similar to that of the mixture of the monomers present in the gas phase, when the content of the monomers which are not propylene of said mixture is comprised within the range of from 2 to 10 mol %.

More particularly, in case of copolymers with ethylene, the ethylene content in the gas-phase mixture is comprised within the range of from 2 to 6 mol %; in case of propylene-ethylene-butene terpolymers, the content of ethylene and butene is comprised within the range of from 2 to 10 mol %. Preferred alpha-olefin comonomers are butene-1, 1-hexene and 4-methyl-1-pentene.

By operating under the above stated conditions, copolymers are obtained, in which the distribution of the comonomers is perfectly homogeneous. This is demonstrated, in case of the copolymers with ethylene, by the analysis by means of ^{13}C-N.M.R.: the presence is not observed of the characteristic signals of the sequences of more than one ethylene units, as described in Macromolecules 10 (3) 536 (1977).

The preparation of the copolymers by using the above stated catalysts is carried out by operating both in the gas phase and in the liquid phase (in the presence of a solvent consisting of an inert hydrocarbon, or in liquid propylene). The composition of the gas phase, comprised within the above stated critical range, is maintained constant during the polymerization. For example, in case of polymerization of propylene-ethylene mixtures by operating in liquid propylene, a constant overpressure of ethylene is maintained.

On the contrary, in case the polymerization is carried out in the gas phase, or in the presence of an inert hydrocarbon solvent, a gaseous mixture of the monomers with a constant composition is fed. The polymerization is carried out at temperatures lower than 20°C, and preferably comprised within the range of from 0° to 10°C.

The copolymers obtained by operating under the above stated conditions have an intrinsic viscosity in tetralin at 135°C higher than 0.2 dl/g. As already stated, the copolymers are mainly used in the field of films; this, thanks to the high weldability characteristics of the films obtained from them.

The following examples are given for the purpose of merely illustrating the invention, without limiting it.

Examples 1 - 8

Polymethylalumoxane synthesis

To a flask of 500 ml of capacity, equipped with thermometer, bubble-condenser with stopcock connected to the gas meter, 100-ml dripping funnel, nitrogen stopcock and magnetic stirrer, 44.5 g of $Al_2(SO_4)_3.18H_2O$ and 200 ml of toluene are charged under a nitrogen atmosphere, and to the dripping funnel 60 ml of pure trimethyl-Al is charged.

The nitrogen supply is discontinued, the connection to the gas meter is opened and, at room temperature, trimethyl-Al is rapidly added dropwise to the suspension of $Al_2(SO_4)_3.18H_2O$, with this latter being kept vigorously stirred.

The temperature rises up to 55°C; it is increased up to 60°C by means of a heating bath, and is maintained constant at this value. The reaction is complete after 4 hours. The suspension is filtered, and the solution is dried: 15.8 g of product, corresponding to a yield of 44%, is obtained.

Cryoscopic average molecular weight 1,160; average oligomerization degree 20.

Zirconium compound synthesis

The synthesis of ethylene-bis-indenyl-$ZrCl_2$ - (EBIZ) and of ethylene-bis(tetrahydroindenyl)-$ZrCl_2$ (EBTHIZ) was carried out according to Journal of Organometallic Chemistry (1985) 288, 63.

Polymerization

All operations were carried out under nitrogen.

To a three-neck flask equipped with bubbling tube, thermometer and gas vent stopcock, with mechanical stirring means, and kept at the controlled temperature of 0°C, a solution of 20 ml of toluene, containing 45 mg of polymethylalumoxane and 0.8 mg of zirconium compound is charged.

After evacuating nitrogen, the gas mixture, the composition of which is specified in the following Table, is continuously added (flow rate 20 litres/hour).

The polymerization time, the catalyst type and the characteristics of the polymer are shown in the Table.

Comparative Example 1

To a glass autoclave of 300 ml, under a propylene stream a solution of 150 ml of toluene containing 350 mg of polymethylalumoxane is

charged, the temperature of the autoclave is adjusted at the controlled value of 0°C, and then 5 mg of EBTHIZ dissolved in toluene is injected. The pressure inside the autoclave is increased up to 4 atm, and the polymerization is allowed to proceed for 4 hours at 0°C. 30.5 g of polymer is obtained, the data of which is reported in the Table.

Comparative Example 2

The process is carried out as in Example 1, with the exception that as the zirconium compound, EBIZ is used (the data relevant to the polymer is reported in the Table).

Comparative Example 3

Example 7 of EP 0 185 938 is repeated, with 20 g being obtained of a polymer which contains 47 mol % of ethylene, with (η) = 0.15 dl/g, and a fraction soluble in xylene at 20°C of 81.3%.

On ^{13}C-N.M.R. investigation, the polymer shows ethylenic sequences.

Table 1

Example N.	Zr Compound	Gas composition (moles %)			Time (hours)	Yield (grams)	Copolymer Composition			(η) (dl/dg)	T (°C)	Fraction soluble in xylene at 20°C % by weight
		C_2	C_4	C_3			C_2	C_4	C_3			
Compar. 1	EBTHIZ	-	-	100	5	30.5	-	-	100	1.25	147	0
Compar. 2	EBIZ	-	-	100	3	4.7	-	-	100	0.68	144	0
1	EBTHIZ	2	-	98	2	1.40	2.6			1.34	134.9	0.16
2	EBIZ	2	-	98	2	0.75	2.8			0.72	132.3	0.0
3	EBTHIZ	3.5	-	96.5	2	3.10	3.5			1.6	129.6	2.5
4	EBIZ	3.5	-	96.5	2	1.90	3.2			0.9	128.1	2.0
5	EBTHIZ	5	-	95	2	1.40	5.4					
6	EBIZ	5	-	95	2	5.25	4.4			0.60	123	2.22
7	EBTHIZ	-	5	95	2	0.48		5.4		1.40	125	5.5
8	EBIZ	-	5	95	2	1.25		5.9		0.46	125	5.3

Claims

Claims for the following Contracting States : BE, DE, FR, GB, NL, SE

1. Crystalline copolymers of propylene with ethylene and/or alpha-olefins

$CH_2 = CHR$

wherein R is an alkyl radical of from 2 to 10 C atoms, containing from 2 to 10 mol % of ethylene and/or alpha-olefin, having a melting point comprised within the range of from 110 to 140°C, and a solubility in xylene at 25°C lower than 10% by weight.

2. Copolymers according to claim 1, containing from 2 to 6 mol % of ethylene, having a melting point comprised within the range of from 120° to 135°C.

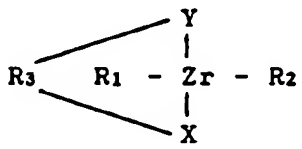
3. Copolymers according to claim 1, containing from 2 to 10 mol % of ethylene and butene.

4. Process for preparing the copolymers according to the preceding claims, comprising polymerizing mixtures of propylene with ethylene and/or alpha-olefins

$CH_2 = CHR$

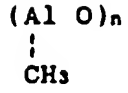
wherein R is an alkyl radical of from 2 to 10 C atoms, with catalysts obtained from:

- stereorigid and chiral compounds of zirconium, of formula:

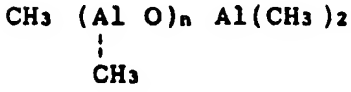


wherein:
R_1 and R_2
are halogens or alkyl groups of from 1 to 6 C atoms or hydrogen;
X and Y
are asymmetrical single-ring or multi-ring organic radicals;
R_3
is a linear radical of from 1 to 4 C atoms, or a cyclic group containing from 3 to 6 C atoms;
and

- either cyclic or linear alumoxanic compounds of formula



wherein n is a numeral comprised within the range of from 2 to 25;
and



wherein n is a numeral comprised within the range of from 1 to 25;
by operating under conditions in which the content of ethylene and/or alpha-olefin present in the mixture in the gas phase is maintained within the range of from 2 to 10 mol %, and the polymerization temperature is lower than 20°C.

Claims for the following Contracting State : ES

1. Process for preparing crystalline copolymers of propylene with ethylene and/or alpha-olefins

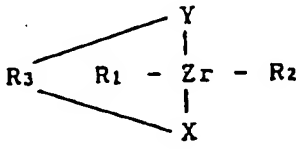
$CH_2 = CHR$

wherein R is an alkyl radical of from 2 to 10 C atoms, containing from 2 to 10 mol % of ethylene and/or alpha-olefin, having a melting point comprised within the range of from 110 to 140°C, and a solubility in xylene at 25°C lower than 10% by weight, comprising polymerizing mixtures of propylene with ethylene and/or alpha-olefins

$CH_2 = CHR$

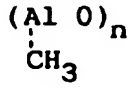
wherein R is an alkyl radical of from 2 to 10 C atoms, with catalysts obtained from:

- stereorigid and chiral compounds of zirconium, of formula:

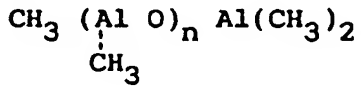


wherein:
R_1 and R_2 are halogens or alkyl groups of from 1 to 6 C atoms or hydrogen;
X and Y are asymmetrical single-ring or

multi-ring organic radicals;
R_3 is a linear radical from 1 to 4 C atoms, or a cyclic group containing from 3 to 6 C atoms;
and
either cyclic or linear alumoxanic compounds of formula



wherein n is a numeral comprised within the range of from 2 to 25;
and



wherein n is a numeral comprised within the range of from 1 to 25;
by operating under conditions in which the content of ethylene and/or alpha-olefin present in the mixture in the gas phase is maintained within the range of from 2 to 10 mol %, and the polymerization temperature is lower than 20 °C.

2. Process according to claim 1, in which copolymers are prepared containing from 2 to 6 mol % of ethylene, having a melting point comprised within the range of from 120 °C to 135 °C.

3. Process according to claim 1, in which copolymers are prepared containing from 2 to 10 mol % of ethylene and butene.

Revendications
Revendications pour les Etats contractants suivants : BE, DE, FR, GB, NL, SE

1. Copolymères cristallins de propylène et d'éthylène et/ou d'alpha-oléfines

$CH_2 = CHR$

dans laquelle R est un radical alkyle comprenant de 2 à 10 atomes de carbone,
contenant de 2 à 10 moles% d'éthylène et/ou d'alpha-oléfine, présentant un moins de fusion compris entre des valeurs de 110 et 140 °C et une solubilité dans le xylène à 25 °C inférieure à 10% en poids.

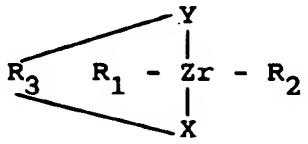
2. Copolymères selon la revendication 1, contenant de 2 à 6 moles% d'éthylène et présentant un point de fusion compris entre des valeurs de 120 et 135 °C.

3. Copolymères selon la revendication 1, contenant de 2 à 10 moles% d'éthylène et de butène.

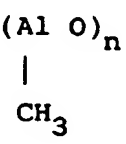
4. Procédé de préparation de copolymères selon les revendications précédentes, consistant à polymériser des mélanges de propylène et d'éthylène et/ou d'alpha-oléfines

$CH_2 = CHR$

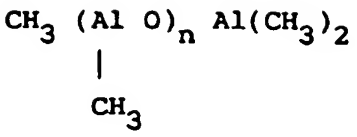
R étant un radical alkyle comprenant de 2 à 10 atomes de carbone;
à l'aide de catalyseurs obtenus à partir:
- de composés stéréorigides et chiraux de zirconium, de formule:



dans laquelle:
R_1 et R_2
sont des atomes d'halogène ou des radicaux alkyles comprenant de 1 à 6 atomes de carbone ou un atome d'hydrogène;
X et Y
sont des radicaux organiques à noyau condensé ou noyau unique asymétrique;
R_3
est un radical linéaire comprenant de 1 à 4 atomes de carbone ou un radical cyclique contenant de 3 à 6 atomes de carbone;
et
- de composés aluminoxaniques soit linéaires, soit cycliques, de formule:



dans laquelle n est un nombre compris entre 2 et 25;
et



dans laquelle n est un nombre compris entre 1 et 25;

en opérant dans des conditions dans lesquelles la teneur en éthylène et/ou alpha-oléfine présents dans le mélange en phase gazeuse est maintenu dans des proportions comprises entre 2 et 10 moles%, et la température de polymérisation est inférieure à 20 °C.

Revendications pour l'Etat contractant suivant : ES

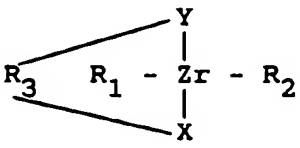
1. Procédé de préparation de copolymères cristallins de propylène et d'éthylène et/ou d'alpha-oléfines

   $CH_2 = CHR$

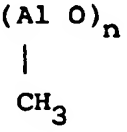
   dans laquelle R est un radical alkyle comprenant de 2 à 10 atomes de carbone,
   contenant de 2 à 10 moles% d'éthylène et/ou d'alpha-oléfine, présentant un moins de fusion compris entre des valeurs de 110 et 140 °C, et une solubilité dans le xylène à 25 °C inférieure à 10% en poids, comprenant la polymérisation des mélanges de propylène et d'éthylène et/ou d'alpha-oléfines

   $CH_2 = CHR$

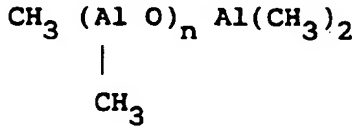
   R étant un radical alkyle comprenant de 2 à 10 atomes de carbone;
   à l'aide de catalyseurs obtenus à partir:
   - de composés stéréorigides et chiraux de zirconium, de formule:



   dans laquelle:
   R_1 et R_2
   sont des atomes d'halogène ou des radicaux alkyles comprenant de 1 à 6 atomes de carbone ou un atome d'hydrogène;
   X et Y
   sont des radicaux organiques à noyau condensé ou noyau unique asymétrique;
   R_3
   est un radical linéaire comprenant de 1 à 4 atomes de carbone ou un radical cyclique contenant de 3 à 6 atomes de carbone;
   et
   - des composés aluminoxaniques soit linéaires, soit cycliques, de formule:



   dans laquelle n est un nombre compris entre 2 et 25;
   et



   dans laquelle n est un nombre compris entre 1 et 25;

   en opérant dans des conditions dans lesquelles la teneur en éthylène et/ou alpha-oléfine présents dans le mélange en phase gazeuse est maintenu dans des proportions comprises entre 2 et 10 moles%, et la température de polymérisation est inférieure à 20 °C.

2. Procédé selon la revendication 1, dans lequel les copolymères sont préparés à partir de 2 à 6 moles% d'éthylène et présentent un point de fusion compris entre des valeurs de 120 et 135 °C.

3. Procédé selon la revendication 1, dans lequel les copolymères sont préparés à partir de 2 à 10 moles% d'éthylène et de butène.

Patentansprüche
Patentansprüche für folgende Vertragsstaaten : BE, DE, FR, GB, NL, SE

1. Kristalline Copolymere von Propylen mit Ethylen und/oder α-Olefinen

   $CH_2 = CHR$

   worin R für einen Alkylrest mit 2 bis 10 Kohlenstoffatomen steht, die 2 bis 10 Mol-% Eth-

ylen und/oder α-Olefin enthalten und einen Schmelzpunkt im Bereich von 110 bis 140 °C sowie eine Löslichkeit in Xylol bei 25 °C von geringer als 10 Gew.-% aufweisen.

2. Copolymere gemäß Anspruch 1, die 2 bis 6 Mol-% Ethylen enthalten und einen Schmelzpunkt im Bereich von 120 bis 135 °C aufweisen.

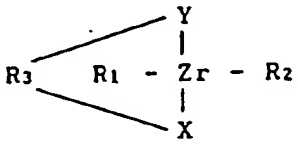
3. Copolymere gemäß Anspruch 1, die 2 bis 10 Mol-% Ethylen und Buten enthalten.

4. Verfahren zur Herstellung der Copolymeren gemäß den vorhergehenden Ansprüchen, umfassend die Polymerisation von Mischungen von Propylen mit Ethylen und/oder α-Olefinen

$CH_2 = CHR$

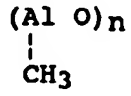
worin R einen Alkylrest mit 2 bis 10 Kohlenstoffatomen bedeutet, mit Katalysatoren, erhalten aus

- sterisch starren und chiralen Verbindungen des Zirconiums der Formel

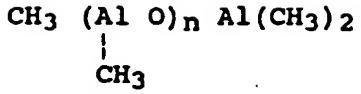


worin
R_1 und R_2 für Halogene oder Alkylgruppen mit 1 bis 6 Kohlenstoffatomen oder Wasserstoff stehen,
X und Y asymmetrische organische Reste mit einem oder mehreren Ringen sind,
R_3 einen linearen Rest mit 1 bis 4 Kohlenstoffatomen oder eine cyclische Gruppe mit 3 bis 6 Kohlenstoffatomen bedeutet,
und

- entweder cyclischen oder linearen Alumoxanverbindungen der Formel



worin n eine Zahl im Bereich von 2 bis 25 ist,
und



worin n eine Zahl im Bereich von 1 bis 25 ist,

indem man unter Bedingungen arbeitet, unter denen der Gehalt an Ethylen und/oder α-Olefin in der Mischung in der Gasphase im Bereich von 2 bis 10 Mol-% gehalten wird, und die Polymerisationstemperatur geringer als 20 °C ist.

Patentansprüche für folgenden Vertragsstaat : ES

1. Verfahren zur Herstellung von kristallinen Copolymeren von Propylen mit Ethylen und/oder α-Olefinen

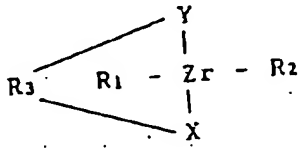
$CH_2 = CHR$

worin R für einen Alkylrest mit 2 bis 10 Kohlenstoffatomen steht, die 2 bis 10 Mol-% Ethylen und/oder α-Olefin enthalten und einen Schmelzpunkt im Bereich von 110 bis 140 °C sowie eine Löslichkeit in Xylol bei 25 °C von geringer als 10 Gew.-% aufweisen, umfassend die Polymerisation von Mischungen von Propylen mit Ethylen und/oder α-Olefinen

$CH_2 = CHR$

worin R einen Alkylrest mit 2 bis 10 Kohlenstoffatomen bedeutet, mit Katalysatoren, erhalten aus

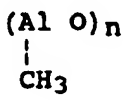
- sterisch starren und chiralen Verbindungen des Zirconiums der Formel



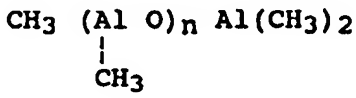
worin
R_1 und R_2 für Halogene oder Alkylgruppen mit 1 bis 6 Kohlenstoffatomen oder Wasserstoff stehen,
X und Y asymmetrische organische Reste mit einem oder mehreren Ringen sind,
R_3 einen linearen Rest mit 1 bis 4 Kohlenstoffatomen oder eine cyclische Gruppe mit 3 bis 6 Kohlenstoffatomen bedeu-

tet,
und

- entweder cyclischen oder linearen Alumoxanverbindungen der Formel



worin n eine Zahl im Bereich von 2 bis 25 ist,
und



worin n eine Zahl im Bereich von 1 bis 25 ist,

indem man unter Bedingungen arbeitet, unter denen der Gehalt an Ethylen und/oder α-Olefin in der Mischung in der Gasphase im Bereich von 2 bis 10 Mol-% gehalten wird, und die Polymerisationstemperatur geringer als 20 °C ist.

2. Verfahren gemäß Anspruch 1, worin Copolymere hergestellt werden, die 2 bis 6 Mol-% Ethylen enthalten und einen Schmelzpunkt im Bereicht von 120 bis 135 °C aufweisen.

3. Verfahren gemäß Anspruch 1, worin Copolymere hergestellt werden, die 2 bis 10 Mol-% Ethylen und Buten enthalten.